



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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(21) International Application Number: PCT/US93/02099 (22) International Filing Date: 8 March 1993 (08.03.93) (30) Priority data: 07/868,041 14 April 1992 (14.04.92) US (71) Applicant: MINNESOTA MINING AND MANUFACTURING COMPANY [US/US]; 3M Center, Post Office Box 33427, Saint Paul, MN 55133-3427 (US). (72) Inventors: SIEDLE, Allen, R. ; LAMANNA, William, M. ; Post Office Box 33427, Saint Paul, MN 55133-3427 (US). (74) Agents: PETERS, Carolyn, V. et al. ; Office of Intellectual Property Counsel, Minnesota Mining and Manufacturing Company, P.O. Box 33427, Saint Paul, MN 55133-3427 (US).	(81) Designated States: AT, AU, BB, BG, BR, CA, CH, CZ, DE, DK, ES, FI, GB, HU, JP, KP, KR, LK, LU, MG, MN, MW, NL, NO, NZ, PL, PT, RO, RU, SD, SE, SK, UA, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, SN, TD, TG).  Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>  (88) Date of publication of the international search report: 20 January 1994 (20.01.94)	
(54) Title: TRIS(PENTAFLUOROPHENYL)BORANE COMPLEXES AND CATALYSTS DERIVED THEREFROM  (57) Abstract  Tris(pentafluorophenyl)borane complexes having the general formula (C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub> B-(YXH) <sub>q</sub> wherein X is oxygen, or sulfur; q is 1 to 3; Y is a hydrogen atom, R <sup>1</sup> -, (R <sup>2</sup> ) <sub>3</sub> Si, or (R <sup>3</sup> ) <sub>2</sub> C=N-; R <sup>1</sup> is a hydrocarbyl group containing 1 to 500 carbon atoms, and may contain a divalent oxygen and further may be a fluorine-containing hydrocarbyl group; R <sup>2</sup> is independently a linear or branched alkyl group containing 1 to 25 carbon atoms, or a phenyl group, further R <sup>2</sup> may contain a SiO- group; and R <sup>3</sup> is independently a hydrocarbyl group containing 1 to 25 carbon atoms, R <sup>3</sup> may be a hydrogen atom provided both R <sup>3</sup> groups selected are not hydrogen atoms; and to complexes containing the borane complexes with an organometallic compound, either as a neutral compound or as an acidic salt that are useful as catalysts for polymerization and copolymerization of olefins and to polymeric products prepared using these catalysts.		

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<b>A. CLASSIFICATION OF SUBJECT MATTER</b> IPC 5 C08F10/00 C07F5/02 C08F4/645 C08F10/14		
According to International Patent Classification (IPC) or to both national classification and IPC		
<b>B. FIELDS SEARCHED</b> Minimum documentation searched (classification system followed by classification symbols) IPC 5 C08F C07F		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practical, search terms used)		
<b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP,A,0 426 637 (FINA TECHNOLOGY, INC) 8 May 1991 see page 4, line 27 - page 5, line 25 ---	11
A	DE,A,12 94 378 (KULZER & CO GMBH) 8 May 1969 see the whole document ---	1-3
A	EP,A,0 443 739 (AIR PRODUCTS AND CHEMICALS) 28 August 1991 see the whole document ---	1
A	EP,A,0 427 697 (FINA TECHNOLOGY, INC) 15 May 1991 see claims 1,17 see example 2 --- -/--	11-22
<input checked="" type="checkbox"/> Further documents are listed in the continuation of box C. <input checked="" type="checkbox"/> Patent family members are listed in annex.		
* Special categories of cited documents : "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubt on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. "A" document member of the same patent family		
Date of the actual completion of the international search  3 December 1993		Date of mailing of the international search report  17. 12. 93
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 1220 HV Rijswijk Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl, Fax (+ 31-70) 340-3016		Authorized officer  Fischer, B

## INTERNATIONAL SEARCH REPORT

International Application No.

PCT/US 93/02099

## C(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
E	WO,A,93 12151 (EXXON CHEMICALS PATENTS INC) 24 June 1993 see examples 3-6,8-12 ---	29
X	WO,A,91 04257 (EXXON CHEMICAL PATENTS INC) 4 April 1991 see examples 35-37 see examples 43,44,57	29
X	see example 36 -----	31

**Box I** Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:  
because they relate to subject matter not required to be searched by this Authority, namely:
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because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
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because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

**Box II** (Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

See PCT/ISA/206 mailed on 27.08.1993

1. ☒ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
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- ☐ The additional search fees were accompanied by the applicant's protest.
- ☒ No protest accompanied the payment of additional search fees.

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A-0426637	08-05-91	CA-A- 2027123 CN-A- 1051311 JP-A- 3207703	01-05-91 15-05-91 11-09-91
DE-A-1294378		BE-A- 715658 CH-A- 494773 FR-A- 1567499 GB-A- 1152421 NL-A- 6807124 US-A- 3558718	16-10-68 15-08-70 16-05-69 21-05-69 25-11-68 26-01-71
EP-A-0443739	28-08-91	GB-A- 2240975	21-08-91
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WO-A-9312151	24-06-93	NONE	
WO-A-9104257	04-04-91	US-A- 5055438 AU-A- 6248390 AU-A- 6443990 CA-A- 2024899 CA-A- 2065745 EP-A- 0420436 EP-A- 0491842 JP-A- 3188092 US-A- 5026798 US-A- 5057475 US-A- 5168111 US-A- 5227440 US-A- 5264405 US-A- 5096867	08-10-91 21-03-91 18-04-91 14-03-91 14-03-91 03-04-91 01-07-92 16-08-91 25-06-91 15-10-91 01-12-92 13-07-93 23-11-93 17-03-92

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(57) Abstract <p>Tris(pentafluorophenyl)borane complexes having the general formula <math>(C_6F_5)_3B(YXH)_q</math> wherein X is oxygen, or sulfur; q is 1 to 3; Y is a hydrogen atom, <math>R^1</math>-, <math>(R^2)_2Si</math>, or <math>(R^3)_2C=N</math>-; <math>R^1</math> is a hydrocarbyl group containing 1 to 500 carbon atoms, and may contain a divalent oxygen and further may be a fluorine-containing hydrocarbyl group; <math>R^2</math> is independently a linear or branched alkyl group containing 1 to 25 carbon atoms, or a phenyl group, further <math>R^2</math> may contain a SiO- group; and <math>R^3</math> is independently a hydrocarbyl group containing 1 to 25 carbon atoms, <math>R^3</math> may be a hydrogen atom provided both <math>R^3</math> groups selected are not hydrogen atoms; and to complexes containing the borane complexes with an organometallic compound, either as a neutral compound or as an acidic salt that are useful as catalysts for polymerization and copolymerization of olefins and to polymeric products prepared using these catalysts.</p>			

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TRIS(PENTAFLUOROPHENYL)BORANE COMPLEXES AND  
CATALYSTS DERIVED THEREFROM

Field of the Invention

5        This invention relates to complex compounds of  
tris(pentafluorophenyl)borane and to mixtures  
containing the borane complexes and an organometallic  
complex that are useful as catalysts for  
polymerization  
10    and copolymerization of olefins and to polymeric  
products prepared using these catalysts.

Background of the Invention

Use of soluble Ziegler-Natta type catalyst  
15    systems in the polymerization of olefins, in  
particular polymerization of ethylene to polyethylene  
is known in the art. In general, traditional Ziegler-  
Natta type systems comprise a transition metal halide  
activated to form a catalyst species by reaction with  
20    a metal alkyl cocatalyst, particularly aluminum alkyl  
cocatalysts. However, aluminum alkyl cocatalysts are  
often used in large excess, see U.S. Patent No.  
4,404,344. This is disadvantageous because the  
aluminum compounds must be removed from the resultant  
25    polymers. These traditional Ziegler-Natta catalysts  
often contain a variety of different active sites,  
each of which has its own rate of initiation,  
propagation, and termination. As a consequence of  
this non-uniformity of active sites, the linear  
30    polyethylene has a broad molecular weight  
distribution. See for example, *Comprehensive  
Organometallic Chemistry*; Wilkinson, G., Ed.; Pergamon  
Press: Oxford, 1982; Vol. 3, Chapter 22.5, p 475;  
*Transition Metals and Organometallics as Catalysts for*  
35    *Olefin Polymerization*; Kaminsky, W. and Sinn, H.,  
Eds.; Springer-Verlag: New York, 1988, and *Transition  
Metal Catalyzed Polymerizations: Alkenes and Dienes*;

Quirk, R.P., Ed.; Harwood: New York 1983.

Recently, catalysts have been reported that rely on boron rather than on aluminum-containing compounds. Boron-based catalysts, in contrast, to the aluminum-based catalysts are often stoichiometric in boron. That is, they contain one mole of boron-containing component per mole of transition metal. Furthermore, it is usually unnecessary to remove the small amount of boron from the polymer, unlike the aluminum-based catalysts, mentioned above.

Tris(pentafluorophenyl)borane ( $C_6F_5$ )<sub>3</sub>B forms 1:1 complexes with Lewis bases such as ether, amines, and phosphines. The compound is hygroscopic and, presumably forms a monohydrate but neither the composition, that is stoichiometry of this hydrate nor its properties have been disclosed. No uses for these donor-acceptor complexes have been taught, see Massey et al. *J. Organomet. Chem.* 1964, 2, 245. Hygroscopic ( $C_6F_5$ )<sub>3</sub>B-Et<sub>2</sub>O was reported by Pohlman et al. *Z. Nat.* 1965, 20b, 5.

Hlatky et al. *J. Am. Chem. Soc.* 1989, 111, 2728 described zwitterionic catalysts such as  $(Me_3Cp)_2Zr[(m-C_6H_4)BPh_3]$ . EPO 0 277 004 describes catalysts prepared by reacting  $(Me_3Cp)_2ZrMe_2$  with  $B_2C_2H_4$ ,  $[Bu_3NH][(B_2C_2H_4)_2Co]$  or  $[Bu_3NH][B_2C_2H_4]$ .

Similarly, EPO 0 418044 describes monocyclopentadienyl complex catalysts containing a non-coordinating, compatible anion such as  $(C_6F_5)_4B^-$ . More recently, homogeneous catalysts exemplified by  $[Cp_2ZrMe][MeB(C_6F_5)_3]$  have been synthesized from the reaction of  $Cp_2ZrMe_2$  and  $(C_6F_5)_3B$  see X. Yang et al. *J. Am. Chem. Soc.* 1991, 113, 3623.

Furthermore, the above described catalysts are sparingly soluble in toluene. The catalysts are even less soluble in normally liquid  $\alpha$ -olefins such as 1-hexene or in mixtures of such olefins and non-reactive solvents, such as hexane, toluene or xylene. These

- catalysts generally separate as oils from toluene or toluene-hexane mixtures. Even though catalysis still proceeds, phase separation is undesirable for several reasons, for example contact between soluble. When
- 5 the catalyst is incompletely soluble, catalyzed polymerization typically takes place at different rates either in solution or at the solid-liquid interface, thus tending to lead to a broad distribution of polymer molecular weights.
- 10 Furthermore, catalyst:monomer ratio in solution is generally difficult to control when the catalyst is only partially soluble.

- It is further known that a soluble or molecularly dispersed catalyst typically permits more ready access
- 15 of the substrate to the active sites. As a result, more efficient use of the catalyst is possible. It is also recognized that the molecular weight of a polymer is proportional to the concentration of monomer in the reaction mixture in which it is synthesized.
- 20 Generally, high molecular weight is desirable in applications such as glues and adhesives, as well as in the construction of rigid objects such as gaskets, insulators and packaging materials.

- Catalytic polymerization of lower olefins, in
- 25 particular ethylene and propylene is relatively easy. On the other hand polymerization of longer chain  $\alpha$ -olefins tends to be slower and the products are often oligomers rather than high polymers, see Skupinska Chem. Rev. 1991, 91, 635. Heterogeneous catalysts
- 30 such as  $\text{TiCl}_4/\text{AlEt}_3$ , which produce higher molecular weight polymers from long-chain  $\alpha$ -olefins, lead to a broad range of molecular weights (high polydispersity index).

Summary of the Invention

Briefly, in one aspect of the present invention catalyst precursor complexes are provided comprising tris(pentafluorophenyl)borane,  $(C_6F_5)_3B$  and at least one  
5 complexing compound such as water, alcohols, mercaptans, silanols, and oximes. These neutral complexes may be converted to acidic salts of their conjugate bases by reaction with amines. The neutral complexes or acidic salts are reacted with Periodic  
10 Table Group IVB organometallic compounds to form catalytically active compounds (hereinafter also referred to as catalysts) useful for polymerization of olefin monomers. Advantageously, the catalysts of the present invention are soluble in olefins to the extent  
15 of  $1 \times 10^{-3}$  molar (M) or greater. Catalysts that can function in undiluted monomer, as distinguished from monomer dissolved in inert diluent, are desirable because the catalysts and monomers tend to produce products having higher molecular weight.  
20 Additionally, because only low levels of the catalysts are used, removal of catalyst or its components from the final, product polymer is generally not required.

Catalysts of the present invention may be used to prepare polyolefins from olefinically unsaturated  
25 monomers having 2 to 30, preferably 5 to 10 carbon atoms. The resulting polymers have a weight average molecular weight of 100,000 to 5,000,000, preferably 500,000 to 3,500,000 and have a polydispersity (PD) of molecular weights  $\leq 3.5$ , preferably 1.5 to 3.  
30 Polymers prepared from long chain  $\alpha$ -olefins having high molecular weight and low polydispersibility are not previously described.

Suitable olefinically unsaturated monomers that may be polymerized using the catalysts of the present  
35 invention include, but are not limited to, linear- and branched  $\alpha$ -olefins, cyclic olefins, olefins containing an aromatic group such as phenyl, olefins

containing silicon and boron, and diolefins. Mixtures of these of monomers, as well as mixtures containing olefins and diolefins may be copolymerized. Preferred unsaturated monomers include linear  $\alpha$ -olefins having the general formula  $C_nH_{2n}$ , where n is 5 to 10.

A feature of the present invention is the incorporation of anions of the type  $YX-B(C_6F_5)_3$  into novel complex salts of Group IVB transition metals (titanium, zirconium, and hafnium), to produce highly active catalysts capable of polymerizing longer chain poly- $\alpha$ -olefins to yield products having very high molecular weights and a narrow polydispersity index. Furthermore, preparation of these salts are described, and such salts can either contain or are essentially free of Lewis bases. An additional feature of this invention is the incorporation of flat carbocyclic ligands into these novel complex salts, to produce olefin polymers of exceptionally high molecular weight. Thus, as shown below using  $[(\text{ligand}),ZrMe][(C_6F_5)_3BOC_{11}H_{17}]$  as the catalyst and 1-hexane as the monomer, polymer molecular weight increases as the ligand is changed in the order of cyclopentadienyl < indenyl << fluorenyl. The fluorenyl ligand is therefore particularly useful when high molecular weight, rubbery polyolefins are desired.

In this application:

- "Cp" means a carbocyclic ligand, such as cyclopentadienyl, indenyl or fluorenyl;
- "Me" means a methyl group;
- "Et" means an ethyl group;
- "Bu" means a butyl group;
- "Ph" means a phenyl group;
- "hydrocarbyl" is used in its usual sense to mean a group containing hydrogen and carbon atoms, such as alkyl, alkenyl, aryl, cycloalkyl, cycloalkenyl,

alkaryl, arylalkyl, and the like; and

"Group IVA" and "Group IVB" are the Periodic Table CAS version designations.

5     Detailed Description of the Preferred Embodiment

The compound  $(C_6F_5)_3B$ .

tris(pentafluorophenyl)borane (also referred to as  
tris(pentafluorophenyl)boron), forms Lewis base  
complexes with a wide variety of alcohols, mercaptans,  
10     silanols, and oximes. These borane complexes are  
catalyst precursors that when combined with Group IVB  
organometallic compounds produce catalysts useful for  
polymerization of olefins, such that the polymers have  
high molecular weights and low polydispersities, that  
15     is a narrow molecular weight distribution.

Lewis base complexes of  $(C_6F_5)_3B$  bearing at least  
one acidic hydrogen atom on the boron-bound heteroatom  
are useful for preparing catalysts. These compounds  
can be represented by the general formula:

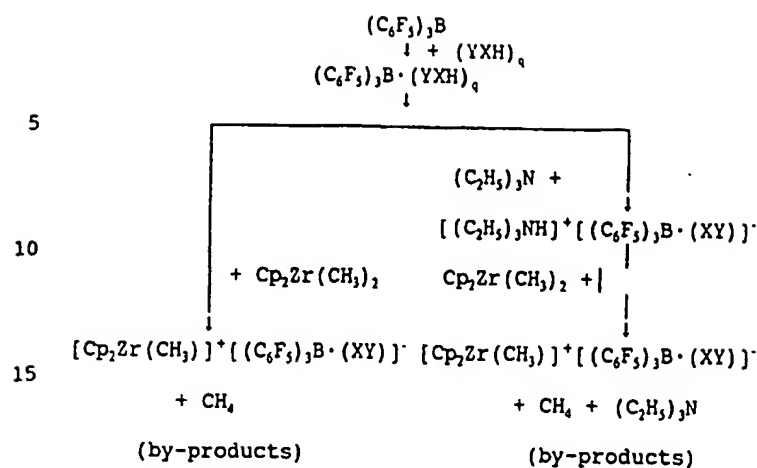
20      $(C_6F_5)_3B \cdot (YXH)_q$  wherein X, Y and q are as described  
below and the valence of X is completed with hydrogen  
atoms where necessary to provide a neutral compound.

The following reaction scheme illustrates how  
neutral Lewis base complexes of

25     tris(pentafluorophenyl)borane and corresponding acidic  
salts may be prepared. For illustration purposes, the  
reaction scheme depicts  $(C_2H_5)_3N$  as a reactant to  
produce acidic salts. Without intending to be bound  
by theory, reaction scheme further illustrates how the  
30     neutral Lewis base complexes of  
tris(pentafluorophenyl)borane and the corresponding  
acidic salts are believed to react with Group IVB  
organometallic complexes to produce the catalytically  
active salts of this invention.

35

7



wherein Y, X, and q are as define below

The neutral borane complexes have the general formula



wherein X is oxygen, or sulfur;

q is 1 to 3, preferably q is 1;

Y is a hydrogen atom, R<sup>1</sup>-, (R<sup>2</sup>)<sub>3</sub>-Si-, or (R<sup>3</sup>)<sub>2</sub>C=N-;

R<sup>1</sup> is a hydrocarbyl group containing 1 to 500,

preferably 1 to 100 carbon atoms, and may contain a divalent oxygen and further may be a halogen-containing hydrocarbyl group, for example the R<sup>1</sup> group can be CH<sub>3</sub>OC<sub>2</sub>H<sub>5</sub>-, t-butylcyclohexyl, isopropyl, allyl, benzyl, methyl, ethyl, C<sub>11</sub>H<sub>27</sub>, oligomeric poly-α-olefins (containing 2 to 100 monomeric units), or CF<sub>3</sub>CF<sub>2</sub>(C<sub>2</sub>F<sub>4</sub>)<sub>n</sub>C<sub>2</sub>H<sub>5</sub>-, where n has an average value of 3.5;

R<sup>2</sup> is independently a linear or branched alkyl group.

containing 1 to 25 carbon atoms, or a phenyl

group, further R<sup>2</sup> may contain a SiO-group, for example (R<sup>2</sup>)<sub>2</sub> may be (t-C<sub>4</sub>H<sub>9</sub>)(CH<sub>3</sub>)<sub>2</sub>- or ((CH<sub>3</sub>)<sub>2</sub>SiO)<sub>2</sub>-; and

R<sup>3</sup> is independently a hydrocarbyl group containing 1 to

25 carbon atoms, further  $R^1$  may be a hydrogen atom provided both  $R^1$  groups selected are not hydrogen atoms, for example when X is oxygen,  $(R^1)_2C=NOH$  forms oximes, a compound (either *cis* or *trans*)  
5 containing the oxime group  $=C=NOH$ ; and is a condensation product of aldehydes or ketones with hydroxylamine.

Tris(pentafluorophenyl)borane tends to form  
10 complexes with alcohols having the general formula  $R^1OH$ . For example, treatment of  $(C_6F_5)_3B$  with methanol liquid or vapor produces the bis(solvate)  $(C_6F_5)_3B \cdot 2MeOH$ . No significant amount of methanol can be removed by pumping at room temperature. This compound can be  
15 converted to  $(C_6F_5)_3B \cdot MeOH$  by treatment with one equivalent of  $(C_6F_5)_3B$ . The 1:1 complex  $(C_6F_5)_3B \cdot MeOH$  may also be prepared by reacting  $(C_6F_5)_3B$  with one equivalent of methanol. Isopropanol forms a bis(solvate) as well but one equivalent of alcohol is removed under vacuum  
20 at room temperature.

Tris(pentafluorophenyl)boron complexes of less volatile alcohols can be prepared by combining one equivalent each of an alcohol and  $(C_6F_5)_3B$  in a suitable, nonreactive solvent such as chloroform or toluene,  
25 followed by evaporation of the solvent. Suitable alcohols contain a wide variety of aliphatic or aromatic groups including but not limited to linear (stearyl alcohol), cyclic (t-butylcyclohexanol), branched (isopropanol), unsaturated (allyl alcohol),  
30 aromatic (benzyl alcohol), optically active (menthol), oxygen-substituted ( $MeOC_2H_4OH$ ), oligomeric (poly-1-hexene alcohol), and halogen-substituted  $[CF_3CF_2(C_2F_5)_nC_2H_4OH]$ , where n has an average value of 3.5.

Suitable alcohols generally have  $pK_a$  values  
35 between -2 and -4. For example, 2,2,2-trifluoroethanol and phenol do not form isorable complexes. Formation of a stable complex is readily ascertained by boron



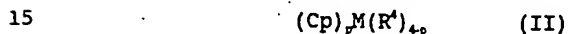
nuclear magnetic resonance ( $^{11}\text{B}$  NMR) spectroscopy. The  $(\text{C}_6\text{F}_5)_3\text{B}$  complexes of this invention have chemical shifts between -5 and + 15 ppm (relative to external  $\text{BF}_3\cdot\text{OEt}_2$ ) compared with +60 ppm for the swung material  $(\text{C}_6\text{F}_5)_3\text{B}$ .

- 5 Other specific examples of  $(\text{YXH})_q$  (when  $q$  is 1) include silanols  $(\text{R}^1)_3\text{SiOH}$ , mercaptans  $(\text{R}^1\text{SH})$ , and oximes  $(\text{R}_1)\text{C}=\text{NOH}$ . Examples of silanols include but are not limited to  $(t\text{-C}_4\text{H}_9)_3\text{SiOH}$  and  $(\text{Me}_3\text{SiO})_3\text{SiOH}$ . Higher mercaptans having low vapor pressures are
- 10 preferred in catalyst applications such that the polymers produced do not have an objectionable odor. An example of a mercaptan useful in the present invention is octadecyl mercaptan. Examples of oximes include acetone oxime and cyclohexanone oxime.
- 15 Of the class of compounds of the type  $(\text{C}_6\text{F}_5)_3\text{B}-(\text{YXH})_q$ , when  $Y$  is hydrogen,  $X$  is oxygen, and  $q$  is 1 or 3, the complex with water is a special case. Exposure of anhydrous  $(\text{C}_6\text{F}_5)_3\text{B}$  to water vapor, produces  $(\text{C}_6\text{F}_5)_3\text{B}\cdot 3\text{H}_2\text{O}$ , a white, stable solid. No intermediate
- 20 hydrate was detected by infrared spectroscopic analysis. The water content was demonstrated by a single crystal X-ray structure determination. Formation of a trihydrate was unexpected because all other previously known  $(\text{C}_6\text{F}_5)_3\text{B}$  complexes with Lewis
- 25 bases have a 1:1 stoichiometry. Vacuum sublimation of the trihydrate produced a mixture of the monohydrate and  $(\text{C}_6\text{F}_5)_3\text{B}$ . The pure monohydrate,  $(\text{C}_6\text{F}_5)_3\text{B}\cdot\text{H}_2\text{O}$ , however may be obtained by combining in organic solvents, such as toluene or chloroform, one equivalent of  $(\text{C}_6\text{F}_5)_3\text{B}\cdot 3\text{H}_2\text{O}$
- 30 with two equivalents of  $(\text{C}_6\text{F}_5)_3\text{B}$  followed by evaporation of the solvent. This conproportionation reaction is a convenient way of synthesizing the monohydrate as needed. Unlike  $(\text{C}_6\text{F}_5)_3\text{B}\cdot 3\text{H}_2\text{O}$ ,  $(\text{C}_6\text{F}_5)_3\text{B}\cdot\text{H}_2\text{O}$  is unstable and slowly decomposes, either in solution or in the solid
- 35 state, to  $(\text{C}_6\text{F}_5)_2\text{BOH}$  and  $\text{C}_6\text{F}_5\text{H}$ . The monohydrate may also be prepared by combining one mole each of water and

$(C_6F_5)_3B$ .

The heteroatom-bound protons in Lewis base complexes of  $(C_6F_5)_3B$ , such as  $(C_6F_5)_3B \cdot R'OH$  and  $(C_6F_5)_3B \cdot R'SH$  are acidic and can be removed by treatment  
 5 with bases such as primary, secondary, or tertiary amines. For example, reaction of  $(C_2H_5)_3N$  with  $(C_6F_5)_3B \cdot 3H_2O$  or  $(C_6F_5)_3B \cdot 2CH_3OH$  produces the acidic salts  $[C_2H_5)_3NH]^+[(C_6F_5)_3BOH]^-$  and  $[Et_3NH]^+[(C_6F_5)_3BOCH_3]^-$  respectively. Preferred bases are triethylamine,  
 10 tributylamine and N,N-dimethylaniline.

Catalysts useful for polymerization of olefinic hydrocarbons may be prepared using the precursor borane complexes and hydrocarbylcyclopentadienyl metal complexes having the general formula:



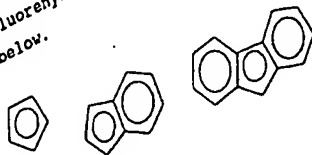
wherein M is titanium, zirconium or hafnium;

p is 1 or 2

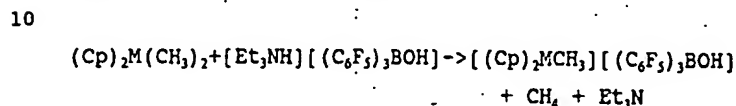
Cp is a cyclopentadienyl ligand, wherein each carbon atom in the ring may be,  
 20 independently, substituted with a radical selected from the group consisting of hydrocarbyl radicals, hydrocarbyl-substituted metalloid radicals wherein the metalloid is selected from Group IVA of the Periodic Table  
 25 of the elements wherein the hydrocarbyl and substituted-hydrocarbyl radicals contain 1 to 20 carbon atoms and can include straight and branched alkyl groups, cyclic hydrocarbon groups, alkyl-substituted cyclic hydrocarbon  
 30 groups, aromatic groups or alkyl-substituted aromatic groups; one or two pairs of adjacent hydrogen atoms of the cyclopentadienyl ligand may be substituted with one or two  $-(CH)_n$  groups to form indenyl or fluorenyl radicals,  
 35 respectively; further, compounds in which one or two methylene rings having the general formula  $(CH_2)_n$ , wherein n is 3 to 6 may be

11  
substituted for two adjacent hydrogen groups  
in the cyclopentadienyl ligand; further, when  
P is 2, the cyclopentadienyl ligands may be  
combined into one bidentate ligand molecule  
by connecting the cyclopentadienyl ligands by  
an organic or organometalloid group; and  
R<sub>4</sub> is independently hydrogen or a hydrocarbyl or  
substituted-hydrocarbyl group containing from  
1 to 20 carbon atoms and may be a straight or  
branched alkyl group, and if sufficiently  
large enough, a cyclic hydrocarbyl group, an  
alkyl-substituted cyclohydrocarbyl group, an  
aromatic group, an aromatics-substituted alkyl  
group (e.g., benzyl), or an alkyl-substituted  
aromatic group and also include  
trisubstituted organometalloid groups of  
Group IVA elements wherein each hydrocarbyl  
group on the metalloid contains from 1 to 20  
carbon atoms.

15  
20 Suitable examples of Cp include but are not  
limited to cyclopentadienyl, indenyl, fluorenyl,  
bis(octahydrofluorenyl), 1,2-bis(1-indenyl)ethane, 1,2-  
bis(tetrahydroindenyl)ethane,  
25 isopropyl(cyclopentadienyl)-1-fluorenyl and 1,3-bis(9-  
fluorene)propane. Chiral metallocenes are also  
suitable and useful when a stereoregular polymer is  
desired. General structures of cyclopentadienyl,  
indenyl and fluorenyl ligands, respectively are  
30 represented below.

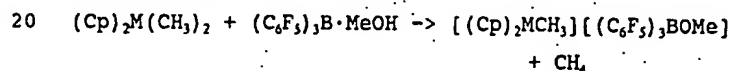


While not intending to be bound by theory, the organometallic complex,  $(Cp)_2M(R')_2$ , is believed to react with acid salts of the anions, such as  $(C_6F_5)_3B \cdot OR^+$ ,  $(C_6F_5)_3B \cdot OH$ ,  $(C_6F_5)_3B \cdot SR^+$ ,  $(C_6F_5)_3B \cdot OSi(R')_3$  or  $(C_6F_5)_3B \cdot ON=C(R')_2$  (containing at least one acid proton in the cationic portion of the salt) to form byproducts and catalytically active salts containing  $(Cp)_2M(R)_2$ . For example, this can be illustrated by the following reaction with  $[EtNH][(C_6F_5)_3BOH]$ .



## (Reaction Scheme I)

Alternatively, the need for an acidic salt can be by-passed in the direct reaction of the metal complexes with neutral complexes of tris(pentafluorophenyl)borane with water, alcohols, mercaptans, silanols or oximes. For example,



## (Reaction Scheme II)

Materials prepared by either route can be used as catalysts for the polymerization of olefins.

Importantly, catalysts prepared according to Reaction Scheme II can be obtained free of extraneous Lewis base byproduct such as triethylamine (obtained in Scheme I).

Materials described in this invention are useful for polymerization of olefins such as ethylene and propylene and in particular higher olefins, for example, 1-hexene or 1-octene. Polyolefins having high weight average molecular weights may be prepared by treating undiluted olefins with a catalytically effective amount of a catalyst of the present invention. Optionally, the polyolefins may be diluted with an inert diluent, such as toluene or hexane.

Catalysts of the present invention may be used to

- prepare polyolefins from olefinically unsaturated monomers having from 2 to 30, preferably 5 to 10 carbon atoms. The resulting polymers have a weight average molecular weight of 100,000 to 5,000,000, preferably 500,000 to 3,500,000 and have a polydispersity (PD) of molecular weights  $\leq 3.5$ , preferably 1.5 to 3. Polymers prepared from longer chain olefins, for example,  $C_nH_{2n}$  ( $n \geq 5$ ) olefins having high molecular weight and low polydispersity have not been previously described.
- 10      Olefinically unsaturated monomers that may be polymerized using the catalysts of the present invention include, but are not limited to, linear- and branched  $\alpha$ -olefins, cyclic olefins, olefins containing an aromatic group such as phenyl, olefins containing
- 15      silicon and boron, and diolefins. Mixtures of these of monomers, as well as mixtures containing olefins and diolefins may be copolymerized.

Tabl 1

P lyhexanes Obtained  
with  
Diff rent Metanocenium Ion Catalysts<sup>(a)</sup>

5

10

15

20

25

Initiator	Degree of Polymerization <sup>(b)</sup>	% Conversion
$\text{Cp}_2\text{ZrMe}^+$	99	100
$(\text{indenyl})_2\text{ZrMe}^+$	200	70
$(\text{Me}_3\text{Cp})_2\text{ZrMe}^+$	83	100
$[(\text{Me}_3\text{Si})_2\text{Cp}]_2\text{HfMe}^+$	66	51
$(\text{Me}_3\text{Cp})_2\text{HfMe}^+$	118	100
$(\text{Me}_3\text{SiCp})_2\text{HfMe}^+$	60	98
$(\text{Me}_3\text{SiCp})_2\text{HfMe}^{+(c)}$	56	90
$\text{Cp}_2\text{HfMe}^+$	429	100
$\text{Cp}_2\text{HfMe}^{+(d)}$	506	100
$(\text{indenyl})_2\text{HfMe}^+$	1025	100
$(\text{Me}_3\text{SiCH}_2\text{Cp})_2\text{ZrMe}^+$	19	4
$(n\text{-C}_4\text{H}_9\text{Cp})_2\text{HfMe}^+$	23	94
$(\text{Me}_3\text{SiCp})_2\text{ZrMe}^+$	10	55
$[\text{Me}_3\text{Si}(\text{C}_6\text{H}_4)_2]_2\text{ZrMe}^+$	4	<1
$(\text{PhCH}_2\text{SiMe}_2\text{Cp})_2\text{ZrMe}^+$	7	88
$(\text{fluorenyl})_2\text{ZrMe}^+$	4800	69
$[(\text{indenyl})_2\text{C}_6\text{H}_4]_2\text{ZrMe}^+$	156	87
$[(\text{indenyl})_2\text{C}_6\text{H}_4]_2\text{HfMe}^+$	271	78

(a) Conditions:  $\text{C}_{10}\text{H}_{17}\text{O} \cdot \text{B}(\text{C}_6\text{F}_5)_3$  salts in 0.5 mL toluene-1-hexene, monomer:catalyst 6400:1 at 0°C

(b) determined by  $^1\text{H}$  NMR analysis and refers to the average number of monomer units in the polymer chain

(c) anion is  $\text{C}_{10}\text{H}_{17}\text{S} \cdot \text{B}(\text{C}_6\text{F}_5)_3$

(d) anion is conjugate base of polyhexene alcohol  $\cdot \text{B}(\text{C}_6\text{F}_5)_3$

35

Ring substitution on the Cp ligand in the catalysts of the present invention can lead to reduced polymer molecular weight and activity. This is illustrated in Table 1. Reduction of polymer molecular weight is generally undesirable in many applications since it is associated with loss of polymer cohesive strength. For example, decreases in molecular weight

40

associated with the Me<sub>3</sub>Si group has not been described before. It is surprising because catalysts prepared from (Me<sub>3</sub>SiCp)<sub>2</sub>ZrMe<sub>2</sub> and methyl aluminoxane tend to produce higher molecular weight polyhexane than does unsubstituted Cp<sub>2</sub>ZrMe<sub>2</sub>.

An advantage of the present invention is the permissible introduction of solubilizing groups that enhance solubility of catalyst salts in the olefinic monomer or solution of monomer and solvent into the anion rather than the cation that contains the active catalytic site. The solubilizing groups are spatially removed from the active site, and therefore do not interfere with polymerization and thus produce polymers of high molecular weight. For example, the catalyst [(indenyl)<sub>2</sub>ZrMe<sub>2</sub>][(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>B·OC<sub>18</sub>H<sub>37</sub>], in which the anion contains the solubilizing octadecyl group that was introduced via of the alcohol Complex (C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>B·C<sub>18</sub>H<sub>37</sub>OH, is soluble to the extent of about 10<sup>-3</sup> M in 80:1 (v/v) 1-hexene-toluene. In an other example, polyhexene alcohol having an average degree of polymerization of 5.9 and bearing a terminal CH<sub>2</sub>OH group, yielded a solution as concentrated as 10<sup>-3</sup> M in 40:1 hexene-hexane. For example, the structure of the solubilizing group can be varied so as to produce good catalyst solubility in a monomer of choice by suitably modifying the structure of R'OH in (C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>B·R'OH. As illustrated in the examples below, the anions of the present invention provide catalysts that produce higher molecular weight polyolefins than superficially related catalysts, even at equivalent monomer: catalyst ratios.

Although (indenyl)<sub>2</sub>ZrMe<sub>2</sub> organometallic compounds are reportedly useful in the preparation of catalysts, there appears to be no correlation between the structure of the ligand(s) in the organometallic portion of the catalyst and the molecular weights of polymers of higher olefins (C5 and greater) produced with such catalysts. As a result, it is not readily

apparent which organometallic compounds may be used to prepare high molecular weight polymers. For example, the soluble, homogeneous olefin polymerization catalysts described by U.S. Patent No. 4,404,344 (Kaminsky et al.) when used to prepare poly(hexene), produces oligomers having molecular weights less than 50,000.

Structurally, flat cyclopentadienyl ligands, when incorporated into these complex salts, produce polymers of high molecular weight. As shown in Table 1 above, using  $[(\text{ligand})_2\text{ZrMe}][(\text{C}_6\text{F}_5)_3\text{B}\cdot\text{OC}_{11}\text{H}_{23}]$  as the catalyst and 1-hexene as the monomer, the degree of polymerization in the product polymer increased from 99 to 200 to 4800 as the ligand was changed in the order from cyclopentadienyl to indenyl to fluorenyl, respectively. The fluorenyl ligand is particularly useful when high molecular weight, rubbery polyolefins are desired.

Objects and advantages of this invention are further illustrated by the following examples, but the particular materials and amounts thereof recited in these examples, as well as other conditions and details, should not be construed to unduly limit the invention.

#### Examples

All compounds were characterized by at least one of infrared (IR) and nuclear magnetic resonance (NMR) spectroscopies. NMR analysis included  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{19}\text{F}$ . Number average molecular weight ( $M_n$ ) and weight average molecular weight ( $M_w$ ) for polymers having  $M_n$  less than  $10^6$  were determined by gel permeation chromatography (GPC) using polystyrene standards or by NMR analysis as is known to those skilled in this art. Polydispersity (PD) refers to the weight-average molecular weight divided by the number average molecular weight, that is,  $M_w/M_n$ .

Materials whose weight average molecular weight



exceeded  $10^6$  were characterized by low angle laser light scattering techniques as is known to those skilled in this art. All starting materials and solvents are commercial available or known in the literature, unless  
5 otherwise stated or apparent. All commercially available materials and solvents are available from Aldrich Chemical Co., unless otherwise noted.

#### Preparation Example 1

##### 10 Preparation of $(C_6F_5)_3B$

Tris(pentafluorophenyl)borane was prepared by the reaction of  $C_6F_5Li$  with  $BCl_3$  in hexane at temperatures below  $-50^\circ C$  according to the procedure described in Massey et al. *J. Organomet. Chem.* 1964, 2, 245.

15

#### Example 1

##### Preparation of $(C_6F_5)_3B \cdot 3H_2O$

A 0.87 gram quantity of  $(C_6F_5)_3B$  was placed in one leg of a reactor consisting of an inverted U-tube,  
20 closed at both ends and fitted with a stopcock and O-ring joint so that the apparatus could be connected to a vacuum line. Excess water was placed in the other leg. After the water had been frozen with a low temperature bath, the apparatus was evacuated. After  
25 warming the reactor to room temperature, the borane reacted with water vapor to form the trihydrate. After water uptake was completed, excess water was pumped away to provide the air-stable product in quantitative yield.

30

#### Example 2

##### Preparation Of $(C_6F_5)_3B \cdot H_2O$

A mixture of 0.566 gram (1 mmol)  $(C_6F_5)_3B \cdot 3H_2O$  as prepared in Example 1 and 1.024 grams (2 mmol)  $(C_6F_5)_3B$   
35 in 10 mL dichloromethane was stirred for 15 minutes and then evaporated to dryness under vacuum. A quantitative yield of the product remained and was

stored under dry nitrogen.

#### Example 3

##### Preparation of $[\text{Et}_3\text{NH}][(\text{C}_6\text{F}_5)_3\text{BOH}]$

- 5 A solution of 3.6 grams  $(\text{C}_6\text{F}_5)_3\text{B} \cdot 3\text{H}_2\text{O}$  as prepared in Example 1 in 20 mL toluene was treated with 0.76 gram triethylamine in 3 mL of the same solvent. The reaction mixture was diluted with 50 mL hexane to precipitate 2.75 gram of crude product. Using Karl
- 10 Fisher analysis, the crude product was determined to be a hydrate and the %  $\text{H}_2\text{O}$  present was 0.66. The crude product was recrystallized by solution in a minimum amount of hot toluene, followed by cooling to  $-50^\circ\text{C}$ . Filtration and vacuum drying yielded a material
- 15 containing 0.15 %  $\text{H}_2\text{O}$  (by weight), corresponding to 5 mole per cent  $\text{H}_2\text{O}$ .

#### Example 4

##### Preparation of $(\text{C}_6\text{F}_5)_3\text{B} \cdot 2\text{MeOH}$

- A solution of 0.34 gram of  $(\text{C}_6\text{F}_5)_3\text{B}$  in 1.5 mL
- 20 methanol was prepared under dry  $\text{N}_2$  and evaporated to dryness to yield a clear viscous residue that crystallized under dynamic vacuum (vacuum pumping) overnight. The yield was 0.33 gram.

#### Example 5

##### Preparation of $[\text{Ph}_3\text{PMe}][(\text{C}_6\text{F}_5)_3\text{BOMe}]$

- A solution of 0.39 gram (0.76 mmol) of  $(\text{C}_6\text{F}_5)_3\text{B}$  in 1 mL methanol was treated with a slight excess (>5%) of
- methanolic sodium methoxide. Excess
- 30 methyltriphenylphosphonium bromide was then added to the solution. The solution was diluted to the cloud point with water and then refrigerated. White crystals were collected on a filter, washed with water and vacuum dried. The yield was 0.58 grams (93%).

Example 6

A similar reaction to Example 5 was used to prepare the triethylammonium salt but, under these conditions, partial hydrolysis of the anion to  $(C_6F_5)_3BOH^-$  occurred.

Example 7**Preparation of  $(C_6F_5)_3B \cdot C_{18}H_{37}OH$** 

A solution of 0.135 gram (0.5 mmol) of 1-octadecanol and 0.256 gram (0.5 mmol) of  $(C_6F_5)_3B$  in 4 mL toluene was stirred for 30 minutes. The solution was then evaporated on a vacuum line. The remaining product was as a viscous oil, and the yield was approximately 0.37 gram. The  $(C_6F_5)_3B$  complex was prepared and handled in an atmosphere of dry nitrogen.

Example 8**Preparation of  $(C_6F_5)_3B \cdot C_{18}H_{37}SH$** 

A solution of 0.143 gram (0.5 mmol) of 1-octadecyl mercaptan and 0.356 gram (0.5 mmol) of  $(C_6F_5)_3B$  in 5 mL dichloromethane was evaporated under high vacuum. The residual product was an oil weighing 0.36 gram.

Example 9**Preparation of  $(C_6F_5)_3B \cdot C_4H_9OC_2H_4OH$** 

A solution of 0.059 gram (0.5 mmol) of 2-butoxyethanol, dried over 4A molecular sieves and 0.256 gram (0.5 mmol) of  $(C_6F_5)_3B$  in 1 mL toluene was evaporated under high vacuum. The residual product was a viscous oil and the yield was approximately 0.24 gram.

Example 10**Preparation of  $(C_6F_5)_3B \cdot \text{cyclo-}C_6H_{10}=\text{NOH}$** 

A solution of 0.056 gram (0.5 mmol) of cyclohexanone oxime and 0.256 gram of  $(C_6F_5)_3B$  in 2.5 mL dichloromethane was evaporated under high vacuum to leave 0.28 gram of product.

Example 11

Preparation of  $(C_6F_5)_3B \cdot (Me_3SiO)_3SiOH$

A solution of 0.312 gram (1 mmol) of tris(trimethylsiloxy)silanol (PCR, Inc., Gainesville, FL) and 0.512 gram (1 mmol) of  $(C_6F_5)_3B$  in 1.5 mL toluene was stirred for 30 minutes and then evaporated under high vacuum. There remaining 0.8 gram of product was a white semi-solid.

Example 12

Fluorinated alcohol complex

Tris(pentafluorophenyl)borane (0.51 gram, 1 mmol) and 0.44 gram (1 mmol) of  $CF_3CF_2(CF_2CF_2)_nCH_2CH_2OH$  (as prepared in U.S. Patent No. 4,219,681, Example 1 and such description is incorporated herein by reference) in which the average value of  $n$  was 3.5 were combined under dry nitrogen in 2 mL of  $CF_2ClCFCl_2$ . After stirring the solution for approximately 1 hour, the solvent was evaporated to leave a fluorinated alcohol complex as a greasy solid.

Example 13

Polymerization using  $(C_6F_5)_3B \cdot H_2O$

1. Preparation of  $(C_3H_5)_2ZrMe_2$

$(C_3H_5)_2ZrMe_2$  was prepared by treatment of  $(C_3H_5)_2ZrCl_2$  in diethyl ether with two equivalents of methyl lithium as described in Samuel et al. *J. Am. Chem. Soc.* 1973, 9, 6263.

2. 1-Hexene (0.67 gram) was added under nitrogen to a catalyst prepared by combining 0.05 mmole each of  $(C_6F_5)_3B \cdot H_2O$  prepared according to Example 2 and  $(C_3H_5)_2ZrMe_2$ . After a few seconds, an exothermic reaction occurred and the mixture became thick. After approximately 50 minutes, any suspended catalyst was removed by centrifugation. Unreacted monomer was then evaporated. NMR ( $^1H$ ) analysis showed that the resultant polymer had a number average molecular weight ( $M_n$ ) of

400. The yield of polymer was 95%.

#### Example 14

Polymerization using  $(M, Cp)HfMe_3$

- 5 1. Preparation of  $(Me_3C_3)HfMe_3$   
 $(Me_3C_3)HfMe_3$  was prepared by reacting  $(Me_3C_3)HfCl_3$  with 3 equivalents of methyllithium as described in Schock et al. J. Am. Chem. Soc. 1988, 110, 7701.
2. A reaction similar to that in the Example 13 was  
10 carried out using  $(Me_3C_3)HfMe_3$  instead of  $(C_3H_5)_2ZrMe_2$ .  
The yield of polymer, with an Mn of 2200, was 90%.

#### Example 15

Polymerization using  $[Et_3NH][(C_6F_5)_3BOH]$

- 15 To 0.31 gram (0.5mmol) of  $[Et_3NH][(C_6F_5)_3BOH]$  (as prepared in Example 3) suspended in 6 mL toluene was added dropwise under dry nitrogen with stirring 0.13 gram (0.5 mmol)  $(C_3H_5)_2ZrMe_2$  (as prepared in Example 13(1)) in 1 mL of the same solvent. Gas evolution  
20 occurred. The resulting orange oil that separated was removed by decantation, washed with toluene, then hexane, and vacuum dried to give 0.31 gram of catalyst as an orange foam.

- This catalyst (0.01 gram) was added under dry  
25 nitrogen to 0.67 gram of 1-hexene. After 3 days, the reaction mixture was diluted with hexane and filtered to remove any undissolved catalyst. Evaporation of the hexane left 0.45 gram of polymer. Gel permeation chromatography (GPC) revealed that the product had  $M_w =$   
30 27,700,  $M_n = 9100$  and PD = 3.04.

#### Example 16

Soluble catalyst prepared using  $(C_6F_5)_3B \cdot C_{18}H_{37}OH$

- 35 A solution of 0.05 mmol  $C_{18}H_{37}OH$  in 0.3 mL toluene was added under dry  $N_2$  to 0.05 mmol of  $(C_6F_5)_3B$ . Then, 0.05 mmol of  $(C_3H_5)_2HfMe_2$  as prepared in Example 14 was added to the solution. Approximately, one half of the

resulting catalyst solution was added with stirring to 13.4 gram dry, oxygen-free 1-hexene that had been cooled to 0°C, the monomer:catalyst ratio was 6400:1. The reaction mixture was essentially clear and transparent, that is, no suspended solids were observed. After approximately 16 hours, the polymer product was removed from the reactor by dissolution in hot heptane. After the heptane had been stripped at 95°C using a water aspirator, 13.6 grams of polymer remained having  $M_w = 148,000$ ,  $M_n = 55,500$  and  $PD = 2.67$ .

#### Examples 17(a) and 17(b)

Reactions similar to Example 16 were carried out using the boron complex prepared according to Example 16 and

(a)  $(Me_3SiC_2H_5)_2HfMe_2$  was prepared by reacting  $Li(Me_3SiC_2H_5)_2$  and  $HfCl_4$  in tetrahydrofuran followed by alkylation with methyllithium. The monomer:catalyst ratio was 6400:1. The resulting polymer had an  $M_n$  of 5040 as determined by NMR analysis; and

(b)  $(n-C_4H_9C_2H_5)_2HfMe_2$  was prepared by reacting  $NaC_4H_9$  in liquid ammonia with 1- $C_4H_9Br$  to provide  $n-C_4H_9C_2H_5$ . This was then converted by reaction with  $n-C_4H_9Li$  and then  $HfCl_4$  to provide  $(n-C_4H_9C_2H_5)_2HfCl_2$ . Subsequent alkylation with methyllithium produced  $(n-C_4H_9C_2H_5)_2HfMe_2$ . The monomer:catalyst ratio was 3200. The resulting polymer had an  $M_n$  of 1932 as determined by NMR analysis.

#### Example 18

Polymerization using oligomeric (polyhexene) alcohol

A reaction like that in Example 16 was carried out using an oligomeric (polyhexene) alcohol (average degree of polymerization 5.9) instead of octadecanol. The oligomeric (polyhexene) alcohol was prepared according to the procedure described in Examples 1a and 1b of co-pending U.S. patent application, Serial No.

07/\_\_\_\_\_, filed April 9, 1992 (Attorney Docket No. 47866USA5A) and such description is incorporated herein by reference. The yield of polymer was essentially quantitative. GPC analysis showed the polymer had  $M_n =$   
5 164,000,  $M_w = 63,000$  and PD = 2.6.

#### Example 19

Comparative example using background art catalyst

Hexene was catalytically polymerized using  
10  $[(C_6H_5)_2HfMe][MeB(C_6F_5)_3]$ , similar to the Zr analogue described in Yang et al. *J. Am. Chem. Soc.* 1991, 113, 3623.

$Cp_2HfMe_2$  and  $(C_6F_5)_3B$  (0.025 mmol each) were combined in 0.7 mL anhydrous toluene in a dry nitrogen  
15 atmosphere. Reaction occurred and a yellow oil separated. The yellow oil was dispersed by shaking and added to 13.4 grams of dry, oxygen-free 1-hexene at 0°C. Separation of a solid catalyst phase was observed. After approximately 48 hours, the resultant  
20 polymer was removed from the reactor by dissolving it in hot cyclohexane. The polymer, after removing the solvents under water aspirator vacuum weighed 13.6 grams (some residual solvent was present). GPC analysis revealed that the polymer had  $M_n = 48,000$ ,  
25  $M_w = 13,500$  and PD = 3.55. The molecular weight of the polymer was lower, and the polydispersity higher than that of the material produced under similar conditions in Example 16.

#### Example 20

Polymerization using  $(C_6F_5)_3B \cdot C_{18}H_{37}SH$

To a solution of 0.05 mmol of the 1-octadecyl mercaptan complex of  $(C_6F_5)_3B$  as prepared in Example 8 was added under nitrogen with stirring 0.024 gram (0.05  
35 mmol) of  $(Me_2SiCp)_2HfMe_2$  in 0.1 mL anhydrous toluene. This mixture was then added to 13.4 grams of dry, oxygen-free 1-hexane. After approximately 48 hours,

the polymer was dissolved in heptane, and then filtered through a pad of granular alumina. After evaporation of the solvent under reduced pressure, there remained 10.2 grams of polymer having an  $M_n$  of 4900 as determined by  $^1\text{H}$  NMR.

#### Example 21

Polymerization using  $(\text{C}_6\text{F}_5)_3\text{B} \cdot (\text{Me}_3\text{SiO})_3\text{SiOH}$

A toluene solution (0.3 mL) containing 0.025 mmol each  $(\text{C}_6\text{F}_5)_3\text{B} \cdot (\text{Me}_3\text{SiO})_3\text{SiOH}$  and (indenyl) $_2\text{HfMe}_2$  as prepared in Example 14 was added with stirring to 13.4 grams of dry, oxygen-free 1-hexene that had been cooled to 0°C. After approximately 16 hours at this temperature, the polymer weighed 23 grams. NMR analysis disclosed that the polymer contained 5 mole % 4-methyl-1-pentene. According to GPC analysis, the polymer had  $M_n = 207,000$ ,  $M_w = 62,000$  and PD 3.3. reactor was opened to air, a small amount of toluene was added and the resulting product scraped into a jar. After the volatiles were removed at 95°C/6.7 hPa (5 mm Hg), 11.3 grams of polymer remained. The polymer had an  $M_w = 340,000$ ,  $M_n = 145,000$  and PD = 2.34.

#### Example 22

Polymerization using  $(\text{C}_6\text{F}_5)_3\text{B} \cdot \text{cyclo-C}_6\text{H}_{10}=\text{NOH}$

A suspension in 0.85 mL toluene of a catalyst prepared from 0.025 mmole each of the  $(\text{C}_6\text{F}_5)_3\text{B} \cdot \text{cyclohexanone oxime complex}$  as prepared in Example 10 and (indenyl) $_2\text{HfMe}_2$  was added with stirring to 13.4 grams of cold (0°C) dry, oxygen-free 1-hexene. After approximately 16 hours, the organic phase was removed and evaporated to give 1.2 grams of polymer having  $M_n$  of 31,000 as determined by NMR analysis.



Example 23

Polymerization using  $(C_6F_5)_3B \cdot BuOC_2H_5OH$

In 0.3 mL anhydrous toluene were combined 0.025 mmole each of the butoxyethanol complex as prepared in Example 9 and  $(indenyl)_2HfMe_2$ . Then 0.67 gram of 1-hexene was added. After approximately 16 hours, the reaction mixture was evaporated to give 0.44 gram (66%) of polymeric product having  $M_n$  of 18,000 as determined by NMR.

10

Example 24

Copolymerization of 1-hexene and 4-methyl-1-pentene

This example illustrates the preparation of a copolymer of two different olefins. A catalyst was prepared from 0.025 mmole each  $(indenyl)_2HfMe_2$  and  $(C_6F_5)_3B \cdot C_{11}H_{27}OH$  as prepared in Example 7 in 0.3 mL of dry, oxygen-free toluene. The catalyst was added with stirring to a mixture of 26.8 grams of dry, oxygen-free 1-hexene and 2.6 grams of 4-methyl-1-pentene that had been cooled to 0°C. After four days, the resulting rigid reaction product was dissolved in 50 mL of toluene and poured into 200 mL of methanol to precipitate the product. After drying in a vacuum oven, the polymer weighed 23 grams. NMR analysis disclosed that the polymer contained 5 mole % 4-methyl-1-pentene. According to GPC analysis, the polymer had  $M_w = 207,000$ ,  $M_n = 62,000$  and PD 3.3.

20

25

Example 25

30 Preparation of high molecular weight polyhexene

A solution of 0.025 mmole  $(fluorenyl)_2ZrMe_2$  (as described in Samuel et al. *J. Organomet. Chem.* 1976, 113, 331) in 0.5 mL of anhydrous toluene was added under  $N_2$  to 0.025 mmole  $(C_6F_5)_3B \cdot C_{11}H_{27}OH$  as prepared in Example 7 in 0.5 mL toluene. The resulting catalyst was added to 13.4 grams of 1-dry, oxygen-free 1-hexene at 0°C. The mixture was too thick to stir with a

35

magnetic stirrer after 10 minutes. After approximately 16 hours, the reactor was opened to air and the contents dissolved in hot toluene. This solution was poured with stirring into a large excess of methanol.

5 After drying in a vacuum oven, the precipitated polymer weighed 9.2 grams. Low angle laser light scattering demonstrated that  $M_n$  was  $2.15 \times 10^6$ . The polydispersity of the polymer was not obtainable because  $M_w$  was not independently known. However, polyhexenes were made

10 using the closely related  $C_{11}H_{17}OB(C_6F_5)_3$  salts of (cyclopentadienyl) $_2$ HfMe<sup>+</sup> and (indenyl) $_2$ HfMe<sup>+</sup>. The polymer polydispersities were 2.7 and 2.6 respectively. These are entries 8 and 10 shown in Table 1. Since polydispersity is essentially unaffected by

15 introduction of one fused benzene ring onto the cyclopentadienyl ligand it is believed the polyhexene prepared according to this and Example 26, wherein the ligand bound to the metal has two fused benzene rings, has a polydispersity of about three or less.

20

#### Example 26

##### High molecular weight polyhexene

A reaction similar to that Example 25 was carried out using less catalyst such that the monomer:catalyst

25 ratio was 37,700:1. Workup was accomplished by scraping the product from the reactor. From 40.2 grams of 1-hexene was obtained 9.8 grams of polymer. Light scattering analysis revealed that  $M_n$  was 3,390,000.

30

#### Example 27

##### Polymerization of 1-octadecene

A solution in 0.5 mL toluene of the catalyst prepared as in Example 24 was added with stirring to 13.4 grams of 1-octadecene at 0°C. After approximately

35 16 hours, the crude product was slurried with warm isopropanol then dried at 160°C/40 Pa (0.3 mm Hg) to give 13.4 grams (85%) of a waxy polymer (m.p. 45°C).

GPC analysis indicated the polymers had a  $M_w = 154,000$ ,  $M_n = 72,000$  and  $PD = 2.14$ .

#### Example 28

##### 5 Copolymerization of 1-hexene and 1,13-tetradecadiene

This example illustrates copolymerization of an olefin and a diolefin. A solution containing 0.025 mmole of the catalyst as prepared as Example 24 was added with stirring to a cold (0°C) mixture of 26.8  
10 (319 mmol) of 1-hexene and 0.17 grams (0.88 mmol) of 1,13- $C_{14}H_{26}$ , (Shell Co., Houston, TX). After approximately 16 hours at this temperature, the insoluble, tough, rubbery polymer was removed from the reactor, cut into small pieces, and then dried at 80°C  
15 under vacuum. The yield was 25.4 grams (94%).

A similar example was run but using instead 0.85 gram of the same diene. The yield of polymer, after vacuum drying, was 25.4 grams (92%).

20

#### Example 29

##### Polymerization of ethylene

In a nitrogen-filled drybox, a solution of 0.05 mmole of (indenyl) $_2$ TiMe $_2$  as prepared according in 0.5 mL toluene was added to 0.05 mmole of  $C_6F_5B \cdot C_{11}H_{27}OH$  in 0.5  
25 mL of the same solvent. The flask was attached to a vacuum line, the contents frozen and the nitrogen pumped away. After thawing, ethylene was admitted until the pressure reached 80 kPa (600 mm Hg). The reactor was stirred and more ethylene was added so as  
30 to maintain the pressure at approximately 80 kPa during the exothermic polymerization. After ethylene consumption had declined, the now-solid reaction mixture was rinsed from the flask with methanol and air dried. The yield of polyethylene, identified by  
35 infrared spectroscopy, was 0.65 gram.

#### Example 30

#### Preparation of poly(cyclop ntene)

This example illustrates the polymerization of a cyclo-olefin. To 14.7 grams of cyclopentene that had been cooled to 0°C was added a solution in 0.4 mL of 5 toluene of the catalyst as prepared in Example 24. The reactor was maintained at this temperature and shaken occasionally. After two days, the mixture was filtered. The solid phase, 1.4 grams, was digested with 50 mL of hot toluene to remove lower molecular 10 weight oligomers and then filtered to provide 0.8 gram of a white, insoluble solid. It was identified by infrared spectroscopy and X-ray powder diffraction as poly(cyclopentene).

Various modifications and alterations of this 15 invention will become apparent to those skilled in the art without departing from the scope and spirit of this invention, and it should be understood that this invention is not to be unduly limited to the illustrative embodiments set fourth herein.

## CLAIMS:

1. A borane complex comprising:
  - (a) tris(pentafluorophenyl)borane and
  - (b) at least one complexing compound
- 5 selected from the group comprising water, alcohol, mercaptan, silanols, and oximes.
  
2. The borane complex according to claim 1, having the general formula:
 
$$(C_6F_5)_3B-(YXH)_q$$
 10 wherein X is oxygen, or sulfur;  
 q is 1 to 3;  
 Y is a hydrogen atom,  $R^1-$ ,  $(R^2)_3Si-$ , or  $(R^3)_3C=N-$ ;  
 15  $R^1$  is a hydrocarbyl group containing 1 to 500 carbon atoms, and may contain a divalent oxygen and further may be a halogen-containing hydrocarbyl group;  
 $R^2$  is independently a linear or branched alkyl  
 20 group containing 1 to 25 carbon atoms, or a phenyl group, further  $R^2$  may contain a SiO-group; and  
 $R^3$  is independently a hydrocarbyl group containing 1 to 25 carbon atoms,  $R^3$  may be a hydrogen  
 25 atom provided both  $R^3$  groups selected are not hydrogen atoms.
  
3. The borane complex according to claim 1, wherein the  $R^1$  group is  $CH_3OC_6H_4-$ , t-butylcyclohexyl,  
 30 isopropyl, allyl, benzyl, methyl, ethyl,  $CF_3CF_2(C_6F_4)_2C_2H_4-$ , where n has an average value of 3.5,  $n-C_{11}H_{23}-$ , or poly- $\alpha$ -olefin oligomer containing 2 to 100 olefin monomer units.
  
- 35 4. The borane complex according to claim 1, wherein Y is  $(t-C_4H_9)((CH_3)_2Si-$  or  $((CH_3)_3SiO)_3Si-$ .

5. The borane complex according to claim 1,  
wherein the borane complex is  $(C_6F_5)_3B \cdot R'OH$ .

6. The borane complex according to claim 1,  
5 wherein the borane complex is  $(C_6F_5)_3B \cdot R'SH$ .

7. The borane complex according to claim 1,  
wherein the borane complex is  $(C_6F_5)_3B \cdot (R^2)_3SiOH$ .

8. The borane complex according to claim 1,  
10 wherein the borane complex is  $(C_6F_5)_3B \cdot (R^3)_2C:NOH$ .

9. The borane complex according to claim 1,  
wherein the borane complex is  $(C_6F_5)_3B \cdot 3H_2O$ .

15 10. The borane complex according to claim 1,  
wherein the borane complex is  $(C_6F_5)_3B \cdot H_2O$ .

11. A catalyst comprising (a) a borane complex  
and (b) a Group IVB organometallic compound.

20

12. The catalyst according to claim 1, wherein  
the borane complex is neutral and has the general  
formula  $(C_6F_5)_3B \cdot (XYH)_q$  and the Group IVB organometallic  
compound has the general formula  $(Cp)_pM(R^d)_q$ .

25 wherein M is titanium, zirconium or hafnium;

X is oxygen, or sulfur;

p is 1 or 2;

q is 1 to 3;

Y is a hydrogen atom,  $R^1-$ ,  $(R^2)_3Si-$ , or  $(R^3)_2C=N-$ ;

30 Cp is a cyclopentadienyl ligand, wherein each  
carbon atom in the ligand may be,  
independently, substituted with a radical  
selected from the group consisting of  
hydrocarbyl radicals, hydrocarbyl-substituted  
35 metalloid radicals wherein the metalloid is  
selected from Group IVA of the hydrocarbyl  
and substituted-hydrocarbyl radicals contain

- 1 to 20 carbon atoms and further can include straight and branched alkyl groups, cyclic hydrocarbon groups, alkylsubstituted cyclic hydrocarbon groups, aromatic groups or alkyl-substituted aromatic groups; one or two pairs of adjacent hydrogen atoms of the cyclopentadienyl ligand may be substituted with one or two  $-(CH)_n$  groups to form indenyl or fluorenyl radicals, respectively, or compounds in which one or two methylene rings having the general formula  $(CH_2)_n$ , wherein n is 3 to 6 in the cyclopentadienyl ligand; further, when p is 2 the cyclopentadienyl ligand may be combined into one bidentate ligand molecule by connecting the cyclopentadienyl ligands by an organic or organometalloid group; and
- $R^1$  is a hydrocarbyl group containing 1 to 500 carbon atoms, and may contain a divalent oxygen and further may be a halogen-containing hydrocarbyl group;
- $R^2$  is independently a linear or branched alkyl group containing 1 to 25 carbon atoms, or a phenyl group, further  $R^2$  may contain a SiO-group; and
- $R^3$  is independently a hydrocarbyl group containing 1 to 25 carbon atoms,  $R^3$  may be a hydrogen atom provided both  $R^3$  groups selected are not hydrogen atoms.
- $R^4$  is independently hydrogen or a hydrocarbyl or substituted hydrocarbyl group containing from 1 to 20 carbon atoms and may be a straight or branched alkyl group, and if sufficiently large enough, a cyclic hydrocarbyl group, an alkyl-substituted cyclohydrocarbyl group, an aromatic group, an aromatic-substituted alkyl group, or an alkylsubstituted aromatic group

and also include trisubstituted organometalloid groups of Group IVA elements wherein each hydrocarbyl group on the metalloid contains from 1 to 20 carbon atoms.

5

13. The catalyst according to claim 12, wherein Cp is a substituted or unsubstituted cyclopentadienyl, indenyl, or fluorenyl group.

10

14. The catalyst according to claim 12, wherein p is 2 and Cp is a cyclopentadienyl group.

15. The catalyst according to claim 12, wherein p is 2 and Cp is a indenyl group.

15

16. The catalyst according to claim 12, wherein p is 1 and Cp is a pentamethyl cyclopentadienyl group.

17. The catalyst according to claim 12, wherein p is 2 and Cp is fluorenyl group.

20

18. The catalyst according to claim 12, wherein XY is an oligomeric O-(poly- $\alpha$ -olefin) group.

19. The catalyst according to claim 12, wherein XY is  $\text{OC}_{11}\text{H}_{27}$ .

25

20. The catalyst according to claim 12, wherein XY is  $\text{SC}_{11}\text{H}_{27}$ .

30

21. The catalyst according to claim 11, wherein the borane complex is an acidic salt wherein the anion has the general formula  $(\text{C}_6\text{F}_5)_3\text{B}\cdot\text{XY}$  and the Group IVB organometallic compound has the general formula

35  $(\text{Cp})_2\text{M}(\text{R}^4)_2$ , wherein M is titanium, zirconium or hafnium.

X is oxygen, or sulfur;



p is 1 or 2;

Y is a hydrogen atom,  $R^1-$ ,  $(R^1)_2Si-$ , or  $(R^1)_2C=N-$ ;

Cp is a cyclopentadienyl ligand, wherein each

carbon atom in the ligand may be,

independently, substituted with a radical

selected from the group consisting of

hydrocarbyl radicals, hydrocarbyl-substituted

metalloid radicals wherein the metalloid is

selected from Group IVA of the periodic table

of the elements, and wherein the hydrocarbyl

and substituted-hydrocarbyl radicals contain

1 to 20 carbon atoms and further can include

straight and branched alkyl groups, cyclic

hydrocarbon groups, alkylsubstituted cyclic

hydrocarbon groups, aromatic groups or alkyl-

substituted aromatic groups; one or two pairs

of adjacent hydrogen atoms of the

cyclopentadienyl ligand may be substituted

with one or two  $-(CH)_n$  groups to form indenyl

or fluorenyl radicals, respectively, or

compounds in which one or two methylene rings

having the general formula  $(CH_2)_n$ , wherein n is

3 to 6 in the cyclopentadienyl ligand;

further, when p is 2 the cyclopentadienyl

ligand may be combined into one bidentate

ligand molecule by connecting the

cyclopentadienyl ligands by an organic or

organometalloid group; and

$R^1$  is a hydrocarbyl group containing 1 to 500

carbon atoms, and may contain a divalent

oxygen and further may be a halogen-

containing hydrocarbyl group;

$R^2$  is independently a linear or branched alkyl

group containing 1 to 25 carbon atoms, or a

phenyl group, further  $R^2$  may contain a SiO-

group; and

$R^3$  is independently a hydrocarbyl group containing

1 to 25 carbon atoms, R<sup>3</sup> may be a hydrogen atom provided both R<sup>3</sup> groups selected are not hydrogen atoms.

5 R<sup>4</sup> is independently hydrogen or a hydrocarbyl or substituted hydrocarbyl group containing from 1 to 20 carbon atoms and may be a straight or branched alkyl group, and if sufficiently  
10 large enough, a cyclic hydrocarbyl group, an alkyl-substituted cyclohydrocarbyl group, an aromatic group, an aromatic-substituted alkyl group, or an alkylsubstituted aromatic group and also include trisubstituted  
15 organometalloid groups of Group IVA elements wherein each hydrocarbyl group on the metalloid contains from 1 to 20 carbon atoms.

22. A method of polymerizing olefinically unsaturated monomers comprising:

(a) contacting at a temperature range within  
20 the range of about -90°C to about 300°C and at a pressure within the range of about 6.9 kPa to 310 MPa (1 to about 45,000 psig) monomers either alone or in combination with one or more monomers in a suitable carrier, solvent or diluent with a catalytically  
25 effective amount of the catalyst according to claim 11, or claim 21.

(b) continuing the contacting of step (a) for a sufficient period of time to polymerize at least a portion of said monomers; and

30 (c) recovering a polymer product.

23. The method according to claim 22, wherein the olefinically unsaturated monomers have from 2 to 30 carbon atoms.

24. The method according to claim 23, wherein the olefinically unsaturated monomers have from 5 to 10 carbon atoms.

5 25. The method according to claim 22, wherein the olefinically unsaturated monomers are selected from the group consisting of linear- and branched  $\alpha$ -olefins, cyclic olefins, olefins containing an aromatic group, olefins containing silicon and boron, diolefins and  
10 mixtures thereof.

26. A polymer prepared according to claim 22, wherein the polymer has a weight average molecular weight of 100,000 to 5,000,000 and a polydispersity  
15 (PD) of molecular weights of less than or equal to 3.5.

27. A polymer prepared according to claim 25, wherein the starting olefinically unsaturated monomer is 1-hexene and the polymer has a weight average  
20 molecular weight of 500,000 to 5,000,000 and a polydispersity of less than 3.5.

28. A polymer prepared according to claim 25, wherein the starting olefinically unsaturated monomer  
25 is 1-octene and the polymer has a weight average molecular weight of 500,000 to 5,000,000 and a polydispersity of less than 3.5.

29. A polymer of a  $C_nH_{2n}$  monomer wherein  $n \geq 5$  and  
30 having weight average molecular weight of 100,000 to 5,000,000 and a polydispersity (PD) of molecular weights of less than or equal to 3.5.

30. A poly(1-hexene) polymer having a weight  
35 average molecular weight of 500,000 to 5,000,000 and a polydispersity of less than 3.5.

31. A poly(1-octene) polymer having a weight average molecular weight of 500,000 to 5,000,000 and a polydispersity of less than 3.5.

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